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(54) Process for electroplating zinc alloy and apparatus employed therefor.

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DERWENT/WPIL, accession no. 87-296109, Derwent Publications Ltd, London, GB; & JP-A-62 208 554 (TANAKA KIKINZOKU KOGYO)

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Description

Background of the Invention

The present invention relates to a process for electro plating a zinc alloy.

In these days, as a surface treated steel having a soft plating surface, stretchablity, good affinity for a paint coating and excellent rust prevention effect which require no heat treatment in a field of automobiles, construction materials, appliances and the like, steels which are electroplated with such an alloy as zinc-iron, zinc-cobalt, zinc-nickel and zinc-manganese have attracted public attention. Zinc-iron plating will be described.

There are two processes for electroplating of a zinc-iron alloy, one of which employs a plating bath containing sulfates of zinc and iron while the other employs a plating bath containing chlorides of zinc and iron. In case of the sulfate bath, such problems exist that liquid resistance is high and the deposition efficiency on a cathode is low because the pH is as low as 1.0. On the other hand, in case of the chloride bath, such advantages exist that liquid resistance is lower than that of the sulfate bath, the deposition efficiency on a cathode is good and the appearance is smooth.

However, in case of the chloride bath, a chlorine gas which is harmful to an anode evolves.

In case of the process for electroplating the zinc-iron alloy in which a titanium electrode plated with iridium or platinum is employed as an anode, the life of the electrode is as short as several thousand hours because the oxygen evolution occurs on the iridium or platinum-plated anode. The valency of the iron ion in the plating bath increases in spite of the supplement of the plating solution because the iron ion is oxidized on the anode. For this reason, the plating solution in the plating bath is circulated to an electrolytic reduction apparatus equipped with an ion exchange membrane to reduce Fe^{3+} to Fe^{2+}. Even by this procedure, the zinc, the iron ion and the pH of the plating bath become unbalanced so that, because the plating thickness may change and part of the surface may become rough, large steel companies discharge about two ton/day of the plating solution that causes serious loss.

In Chem. Abstr., vol 112, no. 6, 05.02.90, page 577, abstr. no. 44303m, N. Mineo and N. Furuya (an inventor of the present application) disclose the plating of a zinc-iron alloy on an iron plate (cathode) by using a hydrogen depolarized gas diffusion anode, in a chloride zinc plating bath. Reportedly, chlorine was not generated and the surface appearance of the plated cathode was excellent. In the document DERWENT/WPIL, accession number 87/296109 corresponding to Japanese application JP-A-62208554, a gas diffusion electrode composed of a laminated film having a reaction layer and a gas diffusion layer bonded together for use in fuel cells, electrochemical reactions and as anodes for electroplating, is disclosed.

Since the steel electroplated with the zinc-iron alloy moves at high speed of 200 m/min. in the small plating bath, the anode cannot be used if the mechanical strength is insufficient. The anode may be scratched and sparks when the anode contacts the steel.

Summary of the Invention

An object of the present invention is to provide a process for electroplating a steel with a zinc alloy using a gas diffusion electrode apparatus which does not require a frequent discharge of the plating solution.

A further object of the invention is to provide a process wherein scratches and sparks are prevented.

The process for electroplating a zinc-iron alloy according to the present invention for overcoming the above problems comprises disposing in an electrolytic cell a gas diffusion electrode apparatus comprising a plurality of gas diffusion electrodes which function as an anode and are formed by a gas diffusion layer and a reaction layer being attached together, and an electroconductive reinforcing frame to which the gas diffusion electrodes are supported; forming a zinc alloy plating bath on the reaction layer side of the electrolytic cell which functions as anode chamber; supplying electricity to the gas diffusion electrodes through the reinforcing frame while supplying a hydrogen gas to the electrolytic cell of the gas diffusion layer side; and electroplating a steel with the zinc alloy by passing the steel as a cathode material through the zinc alloy bath.

Since in the process for electroplating the zinc alloy of this invention the gas diffusion electrode is employed as an anode and the hydrogen gas is supplied to the gas diffusion layer side of the gas diffusion electrode to make an anode reaction of the plating bath to a hydrogen oxidation reaction, no oxygen evolves on the anode in case of the sulfate bath and no chlorine gas evolves on the anode so that a smooth and gorgeous zinc alloy plating layer without burns can be formed on the steel passing through the plating bath. Further, ions in the plating bath such as iron, cobalt, manganese and the like are not oxidized on the anode, and even if they are oxidized on the anode to be contaminated in the plating bath in the form of their ions, these ions are reduced by the gas diffusion electrode to lower their ionic valency so that the zinc ion and the pH of the plating bath are never unbalanced. Accordingly, the plating bath can be effectively employed without the discharge of the plating solution, and the plating thickness of the zinc-iron alloy applied to the steel does not change and the sur-

face does not partially become rough.

Since a plurality of the gas diffusion electrodes are supported in the electroconductive reinforcing frame employed in the process for electroplating such an alloy as zinc-iron, zinc-cobalt, zinc-manganese and the like as mentioned before, the mechanical strength of the gas diffusion electrode functioning as an anode is elevated. Therefore, if the steel moves at high speed in the small plating bath, the gas diffusion electrode is never flapped nor scratched and does not generate a spark.

Brief Description of the Drawings

Figs. 1 a and b show a gas diffusion electrode employed in the process of the present invention, Fig. 1 a being a plan view and Fig. 1 b being an A-A sectional view of Fig. 1 a; and

Fig. 2 shows a zinc-alloy electroplating bath employing the gas diffusion electrode apparatus of Fig. 1.

Detailed Description of the Invention

In the gas diffusion electrode apparatus shown in Figs. 1a and 1b, 1 designates a rectangular gas diffusion electrode. The gas diffusion electrode 1 is formed by a gas diffusion layer 2 and a reaction layer 3 attached together, the gas diffusion layer 2 consisting of hydrophobic carbon black and polytetrafluoroethylene, and the reaction layer 3 consisting of hydrophilic carbon black carrying a platinum catalyst, hydrophobic carbon black and polytetrafluoroethylene. A plurality of the gas diffusion electrodes 1, 10 electrodes in this embodiment, are installed and supported in an electroconductive reinforcing frame made of titanium, copper, stainless and the like, in a lattice reinforcing frame 4 made of titanium in this embodiment. A protection member 5 is formed on the front surface of the reinforcing frame 4 at the reaction layer 3 side of the gas diffusion electrode 1.

A gas diffusion electrode apparatus 9 employing the thus constructed gas diffusion electrode was disposed as an anode in an electrolytic cell 10, and a chloride bath 12 was filled in the cell chamber 11 formed on the reaction layer 3 side of the gas diffusion electrode 1, which defined an anode chamber 13. A hydrogen gas was successively introduced into the cell chamber 13 on the gas diffusion layer 2 side of the gas diffusion electrode 1, from an inlet port 14 so as to successively supply the hydrogen gas to the gas diffusion layer 2 side of the gas diffusion electrode apparatus 9 and to simultaneously discharge the hydrogen gas from the gas diffusion electrode 1 through a discharge port 15 of the cell chamber 13. At the same time, the current was passed to the respective gas diffusion electrodes 1 through the reinforcing frame 4. Under these circumstances, a steel foil 16, as a cathode, was passed through the plating bath 12 of the cell chamber 11 at a relatively high speed.

By using the gas diffusion electrode 1 as an anode while supplying the hydrogen gas to the gas diffusion layer 2 side of the gas diffusion electrode 1 so as to make the anode reaction of the chloride plating bath 12 to be a hydrogen oxidation reaction, no chlorine gas was evolved on the anode. The zinc-iron alloy layer plated on the steel 16 was examined to have a smooth and gorgeous surface, without burns. When the steel was successively passed through the cell to effect the electroplating of the zinc-iron alloy, no iron ion was oxidized on the anode from Fe^{2+} to Fe^{3+}. Even if Fe^{3+} is contaminated in the plating bath 12, the zinc, the iron ion and the pH does not become unbalanced because Fe^{3+} is reduced on the gas diffusion electrode 1 to Fe^{2+}. Accordingly, the circulation of the plating solution of the plating bath 12 to an electrolytic reduction apparatus equipped with an ion exchange membrane is unnecessary, and the plating solution of the plating bath 12 can be effectively used without being discharged. No variation of the thickness of the zinc-iron alloy layer plated on the steel 16 and no partial roughness of the surface is observed.

Since the gas diffusion electrodes 1 functioning as an anode are supported in the reinforcing frame 4, providing a high mechanical strength, the electrodes are not flapped nor bent even when the steel 16 moves in the small plating bath 12 at a speed as high as 200 m/min. The protection member 5 disposed on the front surface of the reinforcing frame 4, prevents the moving steel 16 from contacting the gas diffusion electrode 1 so that scratches and sparks are not produced.

The invention will now be illustrated by Examples which, however, are to be considered a merely exemplary practice of the invention, and not as a limitation.

Example

A gas diffusion electrode 1 having a length of 100 mm and a width of 100 mm was formed by a gas diffusion layer 2 with a thickness of 500 μm and a reaction layer 3 with a thickness of 100 μm, attached together. The gas diffision layer 2 consisted of hydrophobic carbon black of average particle size 420 Å and polytetrafluoroethylene of average particle size 0.3 μm. The reaction layer 3 consisted of hydrophilic carbon black of average particle size 420 Å, carrying a platinum catalyst load of 0.56mg/cm², hydrophobic carbon black of average particle size 420 Å and polytetrafluoroethylene of average particle size 0.3 μm. Ten gas diffusion electrodes 1 were installed and supported in an electroconductive reinforcing frame 4 made of titanium. A protection member 5 was equipped on the front surface of the reinforcing frame 4 at

the reaction layer 3 side of the gas diffusion electrode 1.

As shown in Fig. 2, a gas diffusion electrode apparatus 9 was disposed in an electrolytic cell 10, and a chloride bath 12 consisting of 50g/liter-$FeCl_2 \cdot nH_2O$, 245g/liter-$ZnCl_2$, 1.5g/liter-$NaPH_2O_2$ (pH=3.0) was filled in the cell chamber 11 formed on the reaction layer 3 side of the gas diffusion electrode 1. A hydrogen gas was successively introduced into the cell chamber 13, on the gas diffusion layer 2 side of the gas diffusion electrode 1. At the same time, current was flown to the respective gas diffusion electrodes 1 through the latticed reinforcing frame 4. Under these circumstances, a steel cathode 16 was passed through the plating bath 12 of the cell chamber 11 at a speed of 200m/min., at a current density of 160 A/dm² and a bath voltage of 8.6 V so that the steel 16 was electroplated with a zinc-iron alloy layer having a thickness of 4 μm.

The gas diffusion electrode 1 was employed as an anode while supplying hydrogen gas to the gas diffusion layer 2 side of the gas diffusion electrode 1 so as to make the anode reaction of the chloride plating bath 12 to be a hydrogen oxidation reaction. No chlorine gas was evolved on the anode. The zinc-iron alloy layer plated on the steel 16 was examined to have a smooth and gorgeous surface without burns. When the steel was successively passed to effect the electroplating of the zinc-iron alloy, no iron ion was oxidized on the anode from Fe^{2+} to Fe^{3+}. Even if Fe^{3+} was contaminated in the plating bath 12, the zinc, the iron ion and the pH did not become unbalanced because Fe^{3+} was reduced on the gas diffusion electrode 1 to Fe^{2+}. Accordingly, the circulation of the plating solution of the plating bath an 12 to an electrolytic reduction apparatus equipped with the ion exchange membrane was unnecessary, and the plating solution of the plating bath 12 could be effectively employed without being discharged. No variation of the thickness of the zinc-iron alloy layer plated on the steel 16 and no partial roughness on the surface were observed.

Since the gas diffusion electrodes 1 functioning as an anode were supported in the reinforcing frame 4 so as to elevate the mechanical strength, the electrodes were not flapped nor bent even when the steel 16 moved in the narrow plating bath 12 at a speed as high as 200 m/min. Since the protection member 5 was formed on the front surface of the reinforcing frame 4, the moving steel 16 was never in contact with the gas permeable electrode 1 so that scratches and sparks were not produced.

Similar results were obtained when a sulfate bath was used in place of the chlorine bath.

Claims

1. A process for electroplating a zinc alloy on a steel cathode rapidly moving through a zinc alloy plating bath, in a cell equipped with a gas diffusion anode in the form of laminated film composed of a reaction layer and a gas diffusion layer bonded together, characterized by comprising

   supporting said gas diffusion anode on a latticed electroconductive reinforcing frame and distributing current to said gas diffusion anode through said reinforcing frame;

   preventing a sliding contact of said rapidly moving cathode with an opposing surface of said gas diffusion anode while restraining flapping of said gas diffusion anode by a protective latticed member disposed over said gas diffusion anode and fastened to said supporting reinforcing frame.

2. A process as defined in claim 1, wherein said plating bath is a chloride bath and said steel cathode moves through the bath, at a speed as high as 200 m/min.

Patentansprüche

1. Verfahren zum Elektroplattieren einer Zinklegierung auf eine sich rasch durch ein Zinklegierung-Plattierungsbad bewegende Stahlkathode in einer Zelle, die ausgestattet ist mit einer Gasdiffusionsanode in Gestalt einer aus einer Reaktionsschicht und einer Gasdiffusionsschicht, die aneinander befestigt sind, bestehenden laminierten Schicht,

   dadurch gekennzeichnet,

   daß es aufweist:

   Tragen der Gasdiffusionsanode an einem gitterförmigen, elektrisch leitfähigen, verstärkenden Rahmen und Verteilen von Strom auf die Gasdiffusionsanode durch den verstärkenden Rahmen;

   Verhindern einer gleitenden Berührung der sich schnell bewegenden Kathode mit einer gegenüberliegenden Oberfläche der Gasdiffusionsanode unter Eingrenzung eines Hin- und Herbewegens der Gasdiffusionsanode durch ein schützendes, gitterförmiges Element, das über der Gasdiffusionsanode angeordnet und an dem tragenden, verstärkenden Rahmen befestigt ist.

2. Verfahren nach Anspruch 1, bei dem das Plattierungsbad ein Chlorid-Bad ist und sich die Stahlkathode mit einer Geschwindigkeit bis zu 200 m/min durch das Bad bewegt.

Revendications

1. Procédé de dépôt électrolytique d'un alliage de zinc sur une cathode en acier se déplaçant rapidement à travers un bain de dépôt électrolytique d'alliage de zinc dans une cellule munie d'une anode à diffusion gazeuse ayant la forme d'un film stratifié fait d'une couche de réaction et d'une couche de diffusion des gaz liées ensemble, caractérisé en ce qu'il comprend les étapes consistant à:
   - supporter ladite anode à diffusion gazeuse dans un cadre de renfort électroconducteur à mailles et envoyer un courant à ladite anode à diffusion gazeuse par l'intermédiaire dudit cadre de renfort,
   - empêcher le contact glissant entre ladite cathode qui se déplace rapidement et une surface en vis-à-vis de ladite anode à diffusion gazeuse tout en évitant un pliage de ladite anode à diffusion gazeuse grâce à un élément de protection à mailles placé au-dessus de ladite anode à diffusion gazeuse et fixé audit cadre de renfort et de soutien.

2. Procédé selon la revendication 1, dans lequel ledit bain de dépôt électrolytique est un bain de chlorures et ladite cathode en acier se déplace dans le bain à une vitesse aussi élevée que 200 m/min.

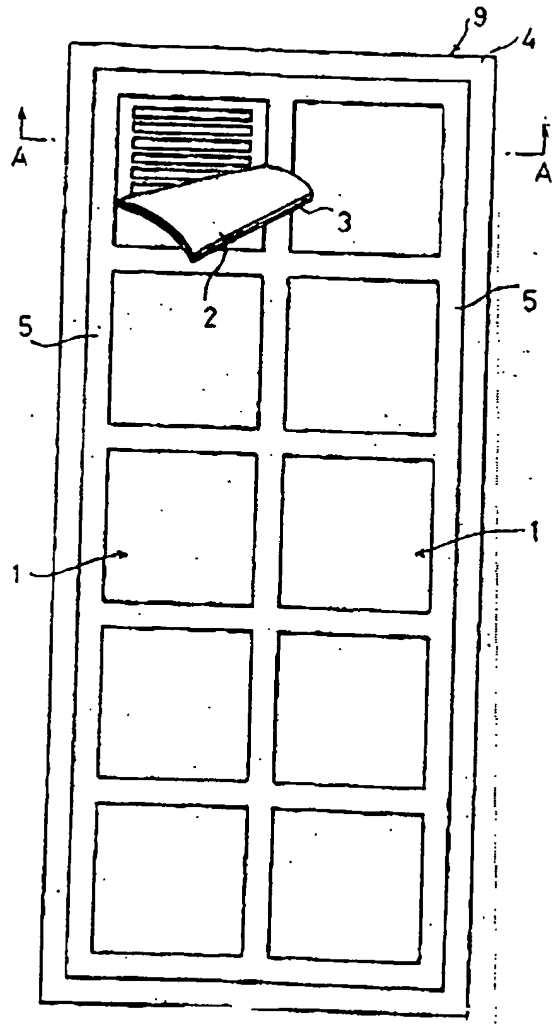

Fig. 1 a

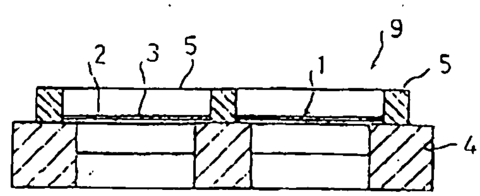

Fig. 1 b

Fig. 2